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Nickel(0)/*N*-heterocyclic carbene complexes catalysed arylation of aromatic diamines

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Abstract

Nickel complexes of *N*-heterocyclic carbenes 'were examined for effecting C–N coupling reactions between aromatic diamines and aryl chlorides of varying electron density. The Ni(0) · 2IPr (IPr = *N*,*N*′-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) complex associated to *t*-BuONa allowed *N*,*N*′-diarylation at 100 °C in 1,4-dioxane with excellent yields. Selective monoarylation of diamines could be performed in THF at 65 °C.

Keywords: *N*-heterocyclic carbenes; Nickel catalysis; C–N coupling; Aromatic diamines; Aryl chlorides

1. Introduction

Arylamines are a class of chemically and biologically important compounds that have a broad spectrum of applications in different fields such as catalysis, medicine and materials [1]. The strong dependence of the physical, chemical and biological properties of arylamines on the nitrogen substituents has prompted great efforts in the synthesis of new arylamines with different electronic and steric environments. The recently developed palladium(0)-catalyzed aryl-nitrogen couplings [2] and the copper-mediated Ullmann couplings [3] are the most commonly used methods for the synthesis of new arylamines. However, despite the numerous applications of palladium- or copper-mediated carbon–nitrogen bond formation reactions, these metal-catalyzed couplings have only scarcely been applied to the arylation of aromatic diamines [4], structural subunit prevalent in the compounds possessing strong electron-donating properties and high stability in the oxidized form which have been investigated for applications such as xerography and organic light-emitting diodes (OLED's) [5]. In most cases, the Pd catalysts employed (generally $Pd(dba)_2/P(t\text{-}Bu)_3$) needed to be used in relatively high loadings (5 mol%) while Cu-catalyzed amination reactions required very high temperatures (200 °C). Due to these disadvantages, S_NAr coupling of fluoronitrobenzenes with arylamines followed by the reduction of the nitro group is still the most common way to prepare aniline oligomers in high yields [6].

In our previous research, we have reported the use of a Ni(0) catalyst associated with a strongly electron donating and sterically hindered *N*-heterocyclic carbene (*N*,*N*′-bis(2,6-diisopropylphenyl)dihydroimidazol-2-ylidene, SIPr, Fig. 1) for the efficient arylation of several classes of amines [7]. The synthesis can be carried out in high yields under mild conditions with a broad variety of aryl chlorides. *N*-heterocyclic carbenes (NHC's) have the general advantage of being better donors than most of tertiary phosphines thereby rendering the oxidative addition of the aryl chloride to nickel facile [8]. The high activity of the SIPr ligand in amination is in part due to its desirable degree of bulk provided by the isopropyl groups which facilitates elimination of the product [9,10]. Prompted by the efficiency of Ni(0)/NHC's catalyst system in amination reactions, we have studied the couplings of aromatic diamines with aryl

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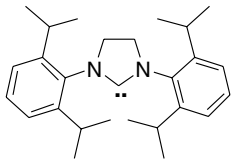


Fig. 1. Structure of the SIPr ligand.

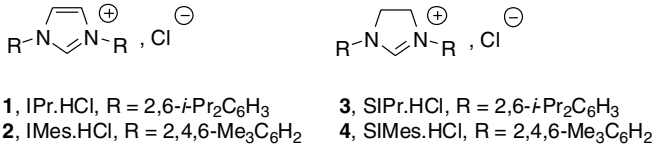


Fig. 2. Structures of carbenes precursors.

chlorides. Herein, we wish to present the details of our study on the selective *N*-mono or *N*,*N*′-diarylation of aromatic diamines with different conjugation length using Ni(0)/NHC's complexes.

2. Results and discussion

2.1. Catalyst preparation

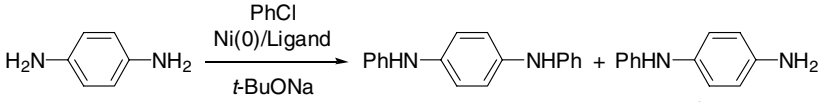
Initially, we investigated the preparation of Ni(0)/*N*-heterocyclic carbene in situ. The catalysts were generated by stirring a mixture of $Ni(acac)_2$ (5 mol%), the imidazolium carbene precursor (10 mol%) and NaH in refluxing 1,4-dioxane followed by the addition of *t*-BuOH. The amount of NaH used was exactly adjusted to reduce the starting Ni(+2) complex into Ni(0) and to convert *t*-BuOH into *t*-BuONa. The role of the in situ generated *t*-BuONa is twofold during the preparation of the NHC bound Ni(0) complex: (a) it initially activates NaH used to reduce $Ni(acac)_2$ into Ni(0), (b) it deprotonates the imidazolium salt to form the carbene ligand which coordinates to the metal. ^{13}C NMR studies directed towards elucidating the Ni(0) · 2IPr catalyst's mode of formation were performed. At room temperature, the signal of the carbene proton (C2) bound to Ni(0) was observed at 219.6 ppm, comparable to the reported chemical shift of the Ni(0) · 2IPr complex prepared from the zerovalent nickel complex $Ni(COD)_2$ (COD = cyclooctadiene), IPr · HCl and *t*-BuOK or from $NiCl_2$, IPr · HCl and *n*-BuLi (respectively 219.4 and 220.5 ppm) [11]. The peak relative to the C2 carbon of the free carbene was not observed in the ^{13}C NMR spectrum. This result indicates that the reduction of $Ni(acac)_2$ and deprotonation of the carbene precursor IPr · HCl are simultaneously caused by *t*-BuONa-activated NaH in a one-pot reaction and that the formation of the Ni(0) · 2IPr complex is effective.

2.2. Synthesis

To select the most effective ligand, 1,4-benzenediamine and chlorobenzene were considered as appropriate substrates for the aryl amination and this combination was tested with various imidazolium and dihydroimidazolium salts (Fig. 2) associated to Ni(0) to determine the optimal conditions for the catalytic *N*,*N*′-diarylation. For this purpose, 1,4-benzenediamine and chlorobenzene (2.4 equiv.) were combined with 1.2 equiv. *t*-BuONa in 1,4-dioxane and allowed to react in the presence of Ni(0) (5 mol%) and the test ligand (10 mol%) for 15 h at 100 °C. The chemical yields and the product ratios were determined by GC/MS (Table 1).

After some experimentation, we found that with carbene precursors **1**–**4**, a 2/1 ratio of carbene to Ni is the best catalyst combination. Increasing the ratio further is highly deleterious, with the essentially complete loss of activity. This tends to imply that the optimum active catalysts, when NHC's are used, are coordinatively unsaturated and that overcoordination effectively "switches-off" the catalysis. Several studies on the catalytic properties of palladium or nickel/carbene complexes have been recently reported and many of them have displayed outstanding levels of activity [9,10,12–14]. Due to the strong interaction between the metal and the carbenic carbon of the imidazole moiety, the metal–carbene bond is robust over time and these catalysts do not require excess ligand to compensate for metal–ligand bond lability. The optimum metal-to-ligand ratio was determined to be 1/1. We suppose that for the diarylation described herein, the catalyst lifetime is increased when

Table 1
Synthesis of *N*,*N*′-diphenyl-1,4-benzenediamine using different NHC ligands[a]



Entry	Ligand	**5** (%)[b]	**6** (%)[b]
a	IPr · HCl **1**	96(92)	3
b	SIPr · HCl **3**	89(85)	8
c	IMes.HCl **2**	13	37
d	SIMes.HCl **4**	11	28

[a] 1,4-Benzenediamine (1 equiv.), Chlorobenzene (2.4 equiv.), Ni(0) (5 mol%), NHC (10 mol%), *t*-BuONa (2.4 equiv.), 100 °C, 1,4-dioxane.
[b] Yields determined by GC unless in parenthesis, which signifies isolated yield (average of at least two runs).

the ratio of Ni/IPr is 1–2. Among the carbenes tested, the bulky 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, generated from IPr · HCl **1** (entry a), was found to be the most effective leading to the formation of *N*,*N*′-diphenyl-1,4-benzenediamine **5** in 92% yield. The use of the dihydroimidazolium carbene SIPr, more σ-donating than IPr [15], decreased the activity and compound **5** was obtained in a slightly lower yield (85%, entry b) using this ligand. Sterically less hindered carbene precursors **2** and **4** afforded the desired compound **5** in poor yields (respectively 13% and 11%, entries c and d).

Nickel(+2) acetylacetonate proved to be the best Ni(0) precursor. $Ni(OAc)_2$ can also be used (63% of **5** after 15 h reaction) while the reaction between 1,4-benzenediamine and chlorobenzene proceeded in a modest 37% yield using $NiCl_2$. When IPr was used as a ligand, there is no advantage in the use of the zerovalent nickel complex $Ni(COD)_2$ compared with $Ni(acac)_2$. The use of the preformed Ni(0) · 2IPr catalyst (from $Ni(COD)_2$ and 2 IPr) shows similar activity to those generated in situ from $Ni(acac)_2$, 2 IPr · HCl and *t*-BuONa-activated NaH. $Ni(acac)_2$ is moreover cheaper and easier to handle than $Ni(COD)_2$.

Dioxane under reflux appears to be the best solvent, whereas THF led to limited levels (less than 30%) of the intermediate *N*-phenyl-1,4-benzenediamine **6** consumption. Other solvents (e.g., toluene) were ineffective. The initial reactions were performed using 1.5 equiv. *t*-BuONa in 1,4-dioxane at 100 °C, as these conditions were found previously to give the best results when aryl aminations were performed with the Ni(0) · SIPr catalyst [7]. However, we found that for the arylation of diamines with the Ni(0) · 2IPr complex, the use of 1.2 equiv. *t*-BuONa in 1,4-dioxane gave much better results, especially at low catalyst loadings. Therefore, the aryl aminations were performed using this solvent/base combination.

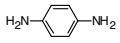
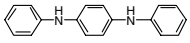
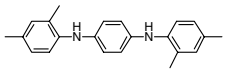
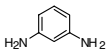
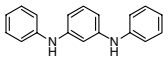
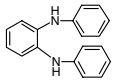
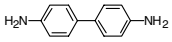
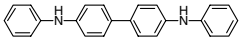
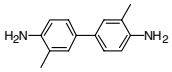
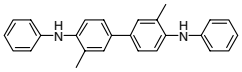
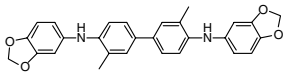
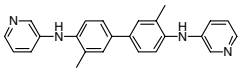
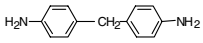
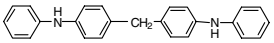
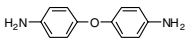
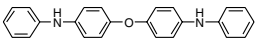
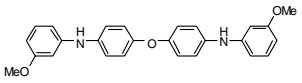
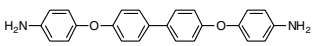
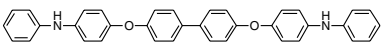
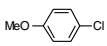
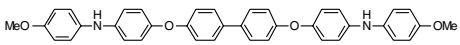
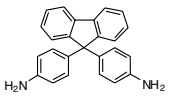
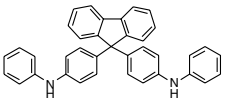
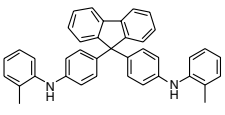
Initial studies were performed using 1,4-, 1,3- and 1,2-phenylene diamines **7**–**9** and chlorobenzene, or 1-chloro-2,4-dimethylbenzene as reactants (Table 2, entries a–d). With diamines **7** and **8**, nearly complete conversions were normally detected in 8 h, but most reactions were allowed to run for 15–20 h to maximize the conversion. Steric hindrance of the aryl chloride does only slightly affect the yield as evidenced when 1-chloro-2,4-dimethylbenzene was used as coupling partner (entry b). However, as anticipated from its steric hindrance, arylation attempt with 1,2-benzenediamine **9** led to no product formation (entry d).

The scope of the Ni(0) · 2IPr-catalyzed *N*,*N*′-diarylation was further investigated. Other diamines, which possess spacers such as biphenyl, phenoxybenzene or benzylbenzene are efficient coupling partners. A catalyst loading of 5 mol% Ni was sufficient to achieve good yields of products, and most of these reactions were completed in less than 20 h. No attempts were made to optimize reaction times. Electron-poor (including 3-chloropyridine), electron-neutral, and electron-rich aryl chlorides were readily aminated with the Ni(0) · 2IPr catalyst system. Electron-withdrawing groups tend to increase reactivity (entries h and k) while electron-rich substrates, such as 4-chloroanisole (entry m), needed more forceful conditions to complete the reaction. Dehalogenation of the starting aryl chloride was only a minor reaction in all cases (less than 2%). No tri- or tetraarylamines, resulting from *N*,*N*- and/or *N*′,*N*′-diarylation, were detected in the reaction mixture under the conditions employed. Using a slight excess of aryl chloride (1.2 equiv. per amine function), only very small amounts of the singly coupled product (generally less than 5%) is formed. The process can be carried out on multigram scale and the final products are easily purified by column chromatography or crystallization. Materials **5**, **16**–**30** exhibit good solubility in numerous common solvents; they are moderately soluble in alcohols and toluene, and extremely soluble in tetrahydrofuran, dichloromethane and chloroform. All compounds **5**, **16**–**30** are stable when they are in the solid state. A rapid oxidation of the phenylenediamine moieties into quinodiimines was however observed when dichloromethane or chloroform solutions of these compounds were exposed to air.

Selective mono-functionalization between two nitrogen atoms in aromatic diamines and especially in phenylene diamines is a useful reaction since this structural subunit is found in numerous natural products and biologically active molecules as well as in industrial dyes or polymers [16]. To the best of our knowledge, Pd-catalyzed amination reactions do not give a general way the monofunctionalization of aromatic diamines. Encouraged by the good results obtained during the *N*,*N*′-diarylation mediated by the Ni(0) · 2IPr complex, we wished to expand the method to the selective *N*-monoarylation of aromatic diamines. To determine the feasibility of this coupling, we first examined the reaction of 1,4-benzene diamine with 1.1 equiv. chlorobenzene in 1,4-dioxane at 100 °C. Under the optimal conditions determined for *N*,*N*′-diarylation, the targeted *N*-phenyl-1,4-benzenediamine **6** was isolated in a modest 43% yield and the symmetrical compound **5** was obtained as by-product in 25% yield. We felt the selective formation of **6** could be achieved by employing milder conditions since GC/MS monitoring of the reaction indicated that the initial coupling was more facile than the second one. After investigating a number of possibilities, we were pleased to find that **6** could be isolated in 72% yield when the coupling was performed in THF for 2 h. Other nonsymmetric fragments may be prepared in good yields using this simple modification of our synthetic methodology (Table 3). The method we developed does not require protection of one of the amine groups and proceeds at low temperature.

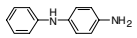
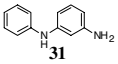
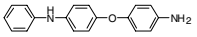
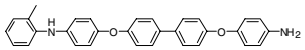
Having demonstrated the viability of the *N*-monoarylation process, we set out to achieve the selective *N*,*N*′-diarylation of aromatic diamines with two different aryl chlorides. Initially, we attempted to prepare unsymmetrical compounds by a one-pot method wherein the second aryl chloride was added after consumption of the first one. However, both steps did not proceed as smoothly as we hoped and attempted couplings provided a complex mixture of products. Apparently, the use of an excess *t*-BuONa

Table 2
N,*N*′-diarylation of aromatic diamines mediated by the Ni(0) · 2IPr catalyst[a]

Entry	Diamine	Aryl chloride	Product	Yield [%][b]
a	 **7**		 **5**	92
b	**7**		 **16**	82
c	 **8**		 **17**	89
d	 **9**		 **18**	0
e	 **10**		 **19**	95
f	 **11**		 **20**	89
g	**11**		 **21**	82
h	**11**		 **22**	95
i	 **12**		 **23**	96
j	 **13**		 **24**	98
k	**13**		 **25**	89
l	 **14**		 **26**	91
m	**14**		 **27**	93
n	 **15**		 **28**	98
o	**15**		 **29**	92
p	**15**		**30**	95

[a] Diamine (1 equiv.), Aryl chloride (2.4 equiv.), Ni(0) · 2IPr (5 mol%), *t*-BuONa (2.4 equiv.), 100 °C, 1,4-dioxane.
[b] Isolated yields (average of at least two runs.

Table 3
Selective *N*-monoarylation of aromatic diamines mediated by the Ni.2IPr catalyst[a]

Entry	Diamine	Aryl chloride	Reaction time [h]	Product	Yield [%][b]
a	**7**		2	 **6**	72
b	**8**		2	 **31**	77
c	**13**		3	 **32**	76
d	**14**		4	 **33**	68

[a] Diamine (1 equiv.), Aryl chloride (1.2 equiv.), Ni(0) · 2IPr (5 mol%), *t*-BuONa (1.2 equiv.), 65 °C, THF.
[b] Isolated yields (average of at least two runs.

(2.4 equiv.) was detrimental to the first coupling and unsymmetrical *N*,*N*′-diaryldiamines were obtained in poor yields, usually less than 20%. We therefore developed a two-step method for the synthesis of the targeted compounds. Monoarylated materials **6**, **31**–**33** were isolated and subjected to a second *N*-arylation reaction catalyzed by the Ni(0) · 2IPr complex in 1,4-dioxane at 100 °C. A variety of electron-rich, -neutral and -deficient aryl chlorides are effectively transformed under these conditions and the unsymmetrical compounds **34**–**37** were obtained in good yields ranging from 68% to 80%.

3. Conclusion

In conclusion, the reactions screened herein indicate that in situ generated Ni(0) bound with the *N*-heterocyclic carbene IPr hold promise as catalyst for C–N bond forming reactions. ^{13}C NMR studies show that mixing 2 equiv. IPr · HCl and Ni(acac)$_2$ in the presence of *t*-BuONa-activated NaH yielded the expected Ni(0) · 2IPr complex. The strong electron donacity and the sterical demand of the IPr ligand lead to catalyst complexes which show good activity for Ni-catalyzed *N*-arylation reactions of aryl chlorides. The Ni(0) · 2IPr allows *N*,*N*′-diarylation or selective *N*-monoarylation of aromatic diamines under mild conditions using readily available and easily handled reagents. A two-step procedure for the synthesis of unsymmetrical *N*,*N*′-diaryl aromatic diamines is also described. Currently work is underway to examine the utility of the Ni(0) · 2IPr complex in other catalytic transformations.

4. Experimental

4.1. General data

Standard Schlenk techniques were used for all reactions. Anhydrous THF and 1,4-dioxane were distilled from sodium/benzophenone. ^{1}H and ^{13}C NMR spectra were obtained either on a Bruker AM 400 or a AC 200 spectrometers. ^{1}H and ^{13}C NMR spectra are reported as positive parts per million (ppm) downfield from a tetramethylsilane (TMS) standard. IR spectra were recorded using NaCl cells or mixtures of compounds/KBr. Mass spectra were obtained on a GC–MS Shimadzu WP-5050 (EI, 70 eV). Melting points were taken on a Tottoli apparatus and were uncorrected. Thin layer chromatography was performed on precoated 5×20 silica gel 60 F_{254} plates (Macherey–Nagel) with detection by UV light. Column chromatography was carried out on Silica gel (E. Merck, 0.063–0.2 mm). Microanalyses were performed at the SRSMC Laboratory, Université Henri Poincaré, France.

t-BuOH was distilled over sodium before use. Ni(acac)$_2$ was purchased from Acros and use as received. Sodium hydride (65% in mineral oil) was purchased from Fluka and used after two washings with anhydrous THF. All diamines and aryl chlorides were purchased from Aldrich Chemicals or TCI Chemicals and used as received.

4.2. Synthesis of the Ni(0) · 2IPr catalyst for *N*,*N*′-diarylation of aromatic diamines

Under a N_2 atmosphere, Ni(acac)$_2$ (0.128 g, 0.5 mmol) and IPr · HCl (0.426 g, 1 mmol) were added in turn to a 50 mL Schlenk flask containing degreased NaH (0.6 g, 25 mmol) in 10 mL anhydrous dioxane. The Schlenk flask was then placed in an oil bath over a magnetic stirring plate set at 100 °C and *t*-BuOH (1.776 g, 24 mmol) in 2 mL dioxane was then injected dropwise. The flask was stirred at 100 °C for 1 h. The Ni(0) · 2IPr catalyst associated to *t*-BuONa thus obtained was directly used for *N*,*N*′-diarylation reactions.

4.3. Representative procedure for the *N*,*N*′-diarylation of aromatic diamines using the Ni(0) · 2IPr catalyst

The aromatic diamine (10 mmol) and the aryl chloride (24 mmol) in 10 mL dioxane were added dropwise over a period of 30 min to the Ni(0) · 2IPr catalyst at 100 °C, and the resultant solution was refluxed under nitrogen. The progress of the reaction was monitored by GC/MS or TLC. After consumption of the starting materials (15–20 h), the flask was cooled to room temperature. Silica gel was added and the solvent was removed in vacuo. The product was purified by column chromatography.

4.3.1. *N*,*N*′-diphenyl-1,4-benzenediamine (**5**)

The title compound was isolated as a brown solid in 92% yield after column chromatography using AcOEt/hexane 5:95 as eluant, m.p. 133 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 7.82 (brs, NH), 7.15 (dd, $J = 7.6$, 7.6 Hz, 4H), 7.03 (s, 4H), 6.96 (d, $J = 7.6$ Hz, 4H), 6.70 (dd, $J = 7.6$, 7.6 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 144.3, 135.9, 128.4, 119.1, 117.6, 114.5. IR (KBr, cm^{-1}): $\nu_{NH} = 3388$. MS (EI) 260. Anal. Calc. for $C_{18}H_{16}N_2$: C, 83.04; H, 6.19; N, 10.76. Found: C, 82.89; H, 6.45; N, 10.50%.

4.3.2. N,N′-di(2,4-dimethylphenyl)-1,4-benzenediamine (**16**)

The title compound was isolated as a beige solid in 82% yield after column chromatography using AcOEt/hexane 3:97 as eluant, m.p. 129 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.99 (d, $J = 7.2$ Hz, 2H), 6.93 (brs, NH), 6.91 (s, 4H), 1.72 (brs, 2H), 6.57 (d, $J = 7.2$ Hz, 2H), 2.17 (s, 6H), 2.16 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 142.9, 137.2, 135.1, 130.4, 123.4, 120.4, 119.7, 116.7, 20.8, 17.5. IR (KBr, cm^{-1}): $\nu_{NH} = 3378$. MS (EI) 316. Anal. Calc. for $C_{22}H_{24}N_2$: C, 83.50; H, 7.64; N, 8.85. Found: C, 83.15; H, 7.83; N, 8.80%.

4.3.3. N,N′-diphenyl-1,3-benzenediamine (**17**)

The title compound was isolated as a clear brown solid in 89% yield after column chromatography using AcOEt/hexane 5:95 as eluant, m.p. 104 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (ddd, $J = 8.0$, 8.0, 1.2 Hz, 4H), 7.11 (dd, $J = 8.0$, 8.0 Hz, 1H), 7.04 (d, $J = 8.0$ Hz, 4H), 6.90 (dd, $J = 8.0$ Hz, 2H), 6.71 (dd, $J = 2.4$ Hz, 1H), 6.60 (dd, $J = 8.0$, 2.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8, 143.3, 130.6, 129.7, 121.5, 118.7, 110.6, 106.7. IR (KBr, cm^{-1}): $\nu_{NH} = 3365$. MS (EI) 260. Anal. Calc. for $C_{18}H_{16}N_2$: C, 83.04; H, 6.19; N, 10.76. Found: C, 83.20; H, 6.30; N, 10.84%.

4.3.4. N-phenyl-4-(4-anilinophenyl)aniline (**19**)

The title compound was isolated as a brown waxy solid in 95% yield after column chromatography using AcOEt/hexane 3:97 as eluant. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25–7.15 (m, 8H), 7.10–6.85 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.7, 142.7, 132.2, 129.1, 128.9, 125.3, 123.6, 122.6, 122.8, 121.9, 118.4. IR (KBr, cm^{-1}): $\nu_{NH} = 3393$. MS (EI) 336. Anal. Calc. for $C_{24}H_{20}N_2$: C, 85.68; H, 5.99; N, 8.33. Found: C, 85.55; H, 6.06; N, 8.52%.

4.3.5. N-phenyl-4-(4-anilino-3-methylphenyl)-2-methylaniline (**20**)

The title compound was isolated as a clear brown solid in 95% yield after column chromatography using AcOEt/hexane 3:97 as eluant, m.p. 123 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (brs, 2H), 7.39–7.30 (m, 4H), 7.25–7.12 (m, 4H), 6.94 (d, $J = 7.6$ Hz, 4H), 6.75 (dd, $J = 7.6$, 7.6 Hz, 2H), 2.28 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.3, 139.70, 132.9, 128.9, 128.5, 128.0, 123.5, 119.1, 118.3, 115.7, 17.71. IR (KBr, cm^{-1}): $\nu_{NH} = 3405$. MS (EI) 364. Anal. Calc. for $C_{26}H_{24}N_2$: C, 85.68; H, 6.64; N, 7.69. Found: C, 85.60; H, 6.83; N, 7.51%.

4.3.6. N-[4-(4-benzo[d][1,3]dioxol-5-ylamino-3-methylphenyl]-2- methylphenyl]benzo[d] [1,3]dioxol-5-amine (**21**)

The title compound was isolated as a brown solid in 82% yield after column chromatography using AcOEt/hexane 30:70 as eluant, m.p. 218 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (brs, 2H), 7.29 (dd, $J = 8.4$, 2.0 Hz, 2H), 7.09 (d, $J = 8.4$ Hz, 2H), 6.74 (d, $J = 8.0$ Hz, 2H), 6.64 (brs, 2H), 6.49 (dd, $J = 8.4$, 2.0 Hz, 2H), 5.93 (s, 4H), 5.22 (brs, NH), 2.29 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.5, 139.3, 138.7, 137.1, 130.3, 126.1, 125.6, 121.8, 115.3, 108.1, 106.2, 98.5, 98.4, 16.3. IR (KBr, cm^{-1}): $\nu_{NH} = 3427$. Anal. Calc. for $C_{28}H_{24}N_2O_4$: C, 74.32; H, 5.35; N, 6.19; O, 14.14. Found: C, 74.57; H, 5.47; N, 6.24%.

4.3.7. N-{2-methyl-4-[3-methyl-4-(3-pyridylamino)phenyl]phenyl}-3-pyridinamine (**22**)

The title compound was isolated as a clear brown solid in 95% yield after column chromatography using MeOH/AcOEt 10:90 as eluant, m.p. 62 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.28 (brs, 2H), 7.97 (brd, $J = 2.8$ Hz, 2H), 7.65 (brs, 2H), 7.50 (brs, 2H), 7.39 (brd, $J = 8.0$ Hz, 2H), 7.23 (brs, 2H), 7.22 (brs, 2H), 7.18–7.13 (m, 2H), 2.29 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 140.8, 139.0, 138.6, 138.0, 133.6, 129.5, 128.2, 123.7, 123.0, 121.0, 119.5, 17.5. IR (KBr, cm^{-1}): $\nu_{NH} = 3244$. MS (EI) 366. Anal. Calc. for $C_{24}H_{22}N_4$: C, 78.66; H, 6.05; N, 15.29. Found: C, 78.43; H, 6.27; N, 15.36%.

4.3.8. N-phenyl-4-(4-anilinobenzyl)aniline (**23**)

The title compound was isolated as a white solid in 96% yield after column chromatography using AcOEt/hexane 5:95 as eluant, m.p. 120 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (ddd, $J = 7.2$, 7.2, 1.2 Hz, 4H), 7.08 (d, $J = 8.4$ Hz, 4H), 7.00 (dd, $J = 7.2$, 1.2 Hz, 4H), 6.99 (d, $J = 8.4$ Hz, 4H), 6.87 (dd, $J = 7.2$, 7.2 Hz, 2H), 5.61 (brs, NH), 3.86 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.9, 139.2, 131.2, 127.3, 127.0, 117.1, 115.4, 114.2, 40.8. IR (KBr, cm^{-1}): $\nu_{NH} = 3389$. MS (EI) 350. Anal. Calc. for $C_{25}H_{22}N_2$: C, 85.68; H, 6.33; N, 7.99. Found: C, 85.70; H, 6.45; N, 7.83%.

4.3.9. N-phenyl-4-(4-anilinophenoxy)aniline (**24**)

The title compound was isolated as a clear brown solid in 98% yield after column chromatography using AcOEt/hexane 10:90 as eluant, mp 123 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.03 (brs, NH), 7.19 (dd, $J = 7.2$, 7.2 Hz, 4H), 7.11 (d, $J = 8.4$ Hz, 4H), 7.03 (d, $J = 8.4$ Hz, 4H), 6.92 (d, $J = 7.2$ Hz, 4H), 6.77 (dd, $J = 7.2$, 7.2 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 150.3, 143.6, 138.0, 128.5, 118.5, 118.4, 118.3, 115.1. IR (KBr, cm^{-1}): $\nu_{NH} = 3403$. MS (EI) 352. Anal. Calc. for $C_{24}H_{20}N_2O$: C, 81.79; H, 5.72; N, 7.95; O, 4.54. Found: C, 81.65; H, 5.60; N, 7.83%.

4.3.10. N-{4-[4-(3-methoxyanilino)phenoxy]phenyl}-3-methoxyaniline (**25**)

The title compound was isolated as a yellow solid in 89% yield after column chromatography using AcOEt/hexane 20:80 as eluant, m.p. 81–82 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.07 (brs, NH), 7.16 (d, $J = 8.4$ Hz, 4H), 7.13 (dd, $J = 8.0$, 8.0 Hz, 2H), 6.96 (d, $J = 8.4$ Hz, 4H), 6.66 (d, $J = 8.0$ Hz, 2H), 6.63 (brs, 2H), 6.37 (d, $J = 8.0$ Hz, 2H), 3.72 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.7, 151.4, 146.0, 138.8, 130.2, 120.0,

119.6, 108.6, 104.7, 101.8, 55.0. IR (KBr, cm^{-1}): $\nu_{NH} = 3410$. Anal. Calc. for $C_{26}H_{24}N_2O_3$: C, 75.71; H, 5.86; N, 6.79; O, 11.64. Found: C, 75.32; H, 6.91; N, 7.00%.

4.3.11. N-phenyl-4-{4-[4-(4-anilinophenoxy)-phenyl]phenoxy}aniline (**26**)

The title compound was isolated as a beige solid in 91% yield after column chromatography using AcOEt/hexane 10:90 as eluant, m.p. 153 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.58–7.47 (m, 4H), 7.23–6.88 (m, 16H), 6.82–6.75 (m, 4H), 6.62 (d, $J = 8.8$ Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 158.7, 157.6, 149.4, 144.2, 140.0, 134.5, 133.6, 129.5, 128.1, 128.0, 121.3, 120.9, 119.6, 119.1, 118.0, 117.1, 116.4, 115.2. IR (KBr, cm^{-1}): $\nu_{NH} = 3414$. Anal. Calc. for $C_{36}H_{28}N_2O_2$: C, 83.05; H, 5.42; N, 5.38; O, 6.15. Found: C, 82.91; H, 5.29; N, 5.47%.

4.3.12. N-(4-methoxyphenyl)-4-{4-[4-(4-methoxyanilino)-phenoxy]phenyl}phenoxy)aniline (**27**)

The title compound was isolated as a clear brown solid in 93% yield after column chromatography using AcOEt/hexane 20:80 as eluant, m.p. 187 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.80 (brs, NH), 7.54 (d, $J = 8.4$ Hz, 2H), 7.52 (d, $J = 8.4$ Hz, 2H), 7.03 (d, $J = 8.4$ Hz, 2H), 7.00–6.89 (m, 12H), 6.85 (d, $J = 8.4$ Hz, 2H), 6.79 (d, $J = 8.4$ Hz, 2H), 6.58 (d, $J = 8.4$ Hz, 2H), 3.71 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 158.1, 157.5, 153.5, 147.6, 145.3, 141.5, 136.4, 133.7, 133.1, 127.5, 127.4, 120.8, 120.6, 119.7, 117.1, 116.6, 116.3, 114.7, 114.3, 55.0. IR (KBr, cm^{-1}): $\nu_{NH} = 3414$. Anal. Calc. for $C_{38}H_{32}N_2O_4$: C, 78.60; H, 5.55; N, 4.82; O, 11.02. Found: C, 78.06; H, 5.39; N, 4.91%.

4.3.13. N-phenyl-4-[9-(4-anilinophenyl)-9H-9-fluorenyl]aniline (**28**)

The title compound was isolated as a beige solid in 98% yield after column chromatography using AcOEt/hexane 5:95 as eluant, m.p. 178 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, $J = 7.2$ Hz, 2H), 7.41 (d, $J = 7.6$ Hz, 2H), 7.33 (dd, $J = 7.2$, 7.2 Hz, 2H), 7.26 (dd, $J = 7.6$, 7.6 Hz, 2H), 7.21 (dd, $J = 7.6$, 7.6 Hz, 4H), 7.10 (d, $J = 8.4$ Hz, 4H), 7.00 (d, $J = 7.6$ Hz, 4H), 6.91 (d, $J = 8.4$ Hz, 4H), 6.87 (dd, $J = 7.6$, 7.6 Hz, 2H), 5.62 (brs, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.9, 142.7, 141.3, 138.8, 136.0, 128.4, 128.3, 127.8, 125.3, 118.8, 116.0, 115.8, 63.2. IR (KBr, cm^{-1}): $\nu_{NH} = 3398$. Anal. Calc. for $C_{37}H_{28}N_2$: C, 88.77; H, 5.64; N, 5.60. Found: C, 88.54; H, 5.56; N, 5.81%.

4.3.14. N-(4-{9-[4-(2-toluidino)phenyl]-9H-9-fluorenyl}phenyl)-2-methylaniline (**29**)

The title compound was isolated as a white solid in 92% yield after column chromatography using AcOEt/hexane 5:95 as eluant, m.p. 196 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, $J = 7.6$ Hz, 2H), 7.42 (d, $J = 7.6$ Hz, 2H), 7.34 (dd, $J = 7.6$, 7.6 Hz, 2H), 7.27 (dd, $J = 7.6$, 7.6 Hz, 2H), 7.20 (d, $J = 8.0$ Hz, 2H), 7.15 (d, $J = 7.6$ Hz, 2H), 7.13–7.06 (m, 6H), 6.87 (dd, $J = 7.2$, 7.2 Hz, 2H), 6.83 (d, $J = 8.6$ Hz, 4H), 5.28 (brs, NH), 2.21 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.3, 142.7, 141.7, 140.7, 138.5, 131.3, 129.5, 128.1, 127.7, 127.1, 126.5, 122.05, 120.5, 118.6, 117.7, 61.9, 18.3. IR (KBr, cm^{-1}): $\nu_{NH} = 3394$. Anal. Calc. for $C_{39}H_{32}N_2$: C, 88.60; H, 6.10; N, 5.30. Found: C, 88.56; H, 6.32; N, 5.05%.

4.3.15. N-(4-methylphenyl)-4-{9-[4-(4-toluidino)phenyl]-9H-fluorenyl}aniline (**30**)

The title compound was isolated as a beige solid in 95% yield after column chromatography using AcOEt/hexane 5:95 as eluant, m.p. 172 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, $J = 7.6$ Hz, 2H), 7.40 (d, $J = 7.6$ Hz, 2H), 7.32 (dd, $J = 7.6$, 7.6 Hz, 2H), 7.25 (dd, $J = 7.6$, 7.6 Hz, 2H), 7.07 (d, $J = 8.8$ Hz, 4H), 7.02 (d, $J = 8.4$ Hz, 4H), 7.02 (d, $J = 8.4$ Hz, 4H), 6.92 (d, $J = 8.4$ Hz, 4H), 6.84 (d, $J = 8.8$ Hz, 4H), 5.52 (brs, NH), 2.26 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.4, 142.8, 140.7, 140.4, 138.1, 131.1, 130.2, 129.5, 128.0, 127.6, 126.5, 120.53, 119.1, 116.9, 64.8, 21.1. IR (KBr, cm^{-1}): $\nu_{NH} = 3395$. Anal. Calc. for $C_{39}H_{32}N_2$: C, 88.60; H, 6.10; N, 5.30. Found: C, 88.76; H, 6.21; N, 5.13%.

4.4. Preparation of the Ni(0) · 2IPr catalyst for selective N-monoarylation of aromatic diamines

The Ni(0) · 2IPr catalyst was prepared as described in Section 4.2 using $Ni(acac)_2$ (0.128 g, 0.5 mmol), IPr · HCl (0.426 g, 1 mmol), NaH (0.312 g, 13 mmol) and *t*-BuOH (0.888 g, 12 mmol) in 10 mL anhydrous THF. The Ni(0) · 2IPr catalyst associated to *t*-BuONa obtained after 1 h heating in THF at 65 °C was directly used for the *N*-arylation reactions.

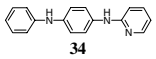
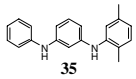
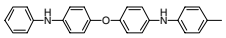
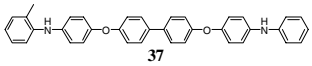
4.5. Representative procedure for the selective N-monoarylation of aromatic diamines using the Ni(0) · 2IPr catalyst

The aromatic diamine (10 mmol) and the aryl chloride (12 mmol) in 10 mL THF were added dropwise over a period of 30 min to the Ni(0) · 2IPr catalyst at 65 °C, and the resultant solution was refluxed under nitrogen for the time indicated in Table 3. The progress of the reaction was monitored by GC/MS or TLC. After cooling to room temperature, silica gel was added and the solvent was removed in vacuo. The product was purified by column chromatography (see Table 4).

4.5.1. N-phenyl-1,4-benzenediamine (**6**)

The title compound was isolated as a brown solid in 72% yield after column chromatography using AcOEt/hexane 20:80 as eluant, m.p. 70 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (dd, $J = 7.2$, 7.2 Hz, 2H), 6.90 (d, $J = 8.4$ Hz, 2H), 6.79 (d, $J = 8.4$ Hz, 2H), 6.75 (dd, $J = 7.2$, 7.2 Hz, 1H), 6.56 (d, $J = 7.2$ Hz, 2H), 5.40 (brs, NH), 3.43 (brs, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.7, 141.8, 133.5, 129.0, 122.9, 118.6, 115.9, 114.8. IR (KBr, cm^{-1}):

Table 4
Synthesis of unsymmetrical *N,N′*-diaryldiamines using the Ni.2IPr catalyst[a]

Entry	Starting material	Aryl chloride	Reaction time [h]	Product	Yield [%][b]
a	**6**		2	 **34**	80
b	**31**		2	 **35**	77
c	**32**		3	 **36**	76
d	**33**		4	 **37**	68

[a] Amine (1 equiv.), Aryl chloride (1.2 equiv.), Ni(0) · 2IPr (5 mol%), *t*-BuONa (1.2 equiv.), 100 °C, 1,4-dioxane.
[b] Isolated yields (average of at least two runs.

$\nu_{NH} = 3400, 3355$. MS (EI) 184. Anal. Calc. for $C_{12}H_{12}N_2$: C, 78.23; H, 6.57; N, 15.21. Found: C, 78.10; H, 6.70; N, 14.96.

4.5.2. N-phenyl-1,3-benzenediamine (**31**)

The title compound was isolated as a brown solid in 77% yield after column chromatography using AcOEt/hexane 20:80 as eluant, m.p. 68 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 7.18 (dd, $J = 7.6$, 7.6 Hz, 2H), 7.03–6.92 (m, 3H), 6.86 (dd, $J = 7.6$, 7.6 Hz, 1H), 6.38 (d, $J = 7.6$ Hz, 1H), 6.23 (s, 1H), 6.15 (d, $J = 7.6$ Hz, 1H), 5.63 (brs, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.2, 143.9, 142.8, 129.8, 129.0, 120.5, 117.9, 107.9, 107.8, 103.9. IR (KBr, cm^{-1}): $\nu_{NH} = 3411$, 3378. MS (EI) 184. Anal. Calc. for $C_{12}H_{12}N_2$: C, 78.23; H, 6.57; N, 15.21. Found: C, 78.33; H, 6.69; N, 14.85%.

4.5.3. N-phenyl-4-(4-aminophenoxy)aniline (**32**)

The title compound was isolated as a brown solid in 76% yield after column chromatography using AcOEt/hexane 25:75 as eluant, m.p. 98 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.16 (dd, $J = 7.4$, 7.4 Hz, 2H), 6.98–6.73 (m, 9H), 6.54 (d, $J = 8.8$ Hz, 2H), 6.53 (brs, NH), 3.41 (brs, NH); ^{13}C NMR (50 MHz, $CDCl_3$): δ 153.5, 149.7, 144.6, 142.5, 137.8, 129.6, 121.1, 120.8, 120.7, 120.5, 120.2, 118.9, 116.5. IR (KBr, cm^{-1}): $\nu_{NH} = 3393$, 3327. MS (EI) 276. Anal. Calc. for $C_{18}H_{16}N_2O$: C, 78.24; H, 5.84; N, 10.14; O, 5.79. Found: C, 77.95; H, 5.71; N, 10.36%.

4.5.4. N-(4-{4-[4-(4-aminophenoxy)phenyl]phenoxy}-phenyl)-2-methylaniline (**33**)

The title compound was isolated as a brown solid in 68% yield after column chromatography using AcOEt/hexane 25:75 as eluant, m.p. 79–80 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.47 (d, $J = 6.8$ Hz, 2H), 7.45 (d, $J = 6.8$ Hz, 2H), 7.19–6.88 (m, 14H), 6.72–6.64 (m, 2H), 2.26 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 158.7, 157.9, 151.2, 149.0, 143.2, 142.4, 140.1, 135.6, 135.0, 131.3, 128.6, 128.5, 128.4, 127.5, 127.2, 121.7, 121.6, 121.0, 120.9, 120.8, 120.4, 118.9, 118.5, 117.9, 117.7, 117.3, 18.3. IR (KBr, cm^{-1}): $\nu_{NH} = 3368$. Anal. Calc. for $C_{31}H_{26}N_2O_2$: C, 81.20; H, 5.72; N, 6.11; O, 6.98. Found: C, 81.17; H, 5.63; N, 5.97%.

4.6. Representative procedure for the synthesis of unsymmetrical N,N′-diaryl aromatic diamines using the Ni(0) · 2IPr catalyst

A 25 mL flask equipped with a stirbar was charged with the Ni(0) · 2IPr catalyst (0.25 mmol Ni(0) and 0.5 mmol IPr), *t*-BuONa (6 mmol), the *N*-monoarylated diamine (5 mmol) and the requisite aryl chloride (6 mmol). The components were heated at 100 °C in 10 mL dioxane for 15–20 h. After cooling to room temperature, silica gel was added and the solvent was removed in vacuo. The product was purified by column chromatography.

4.6.1. N-phenyl-N′-(2-pyridyl)-1,4-benzenediamine (**34**)

The title compound was isolated as a brown solid in 80% yield after column chromatography using AcOEt/hexane 15:85 as eluant, m.p. 62 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (brs, 1H), 7.53 (brs, 1H), 7.24 (brs, 2H), 7.12–6.95 (m, 6H), 6.88 (d, $J = 7.2$ Hz, 2H), 5.92 (brs, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.1, 148.2, 141.2, 137.3, 129.2, 128.7, 120.9, 118.6, 117.8, 117.6, 116.4. IR (KBr, cm^{-1}): $\nu_{NH} = 3389$. MS (EI) 261. Anal. Calc. for $C_{17}H_{15}N_3$: C, 78.13; H, 5.79; N, 16.08. Found: C, 78.01; H, 5.62; N, 16.25%.

4.6.2. N-(2,4-dimethylphenyl)-N′-phenyl-1,3-benzenediamine (**35**)

The title compound was isolated as a waxy brown solid in 80% yield after column chromatography using AcOEt/hexane 5:95 as eluant. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (dd, $J = 7.6$, 7.6 Hz, 2H), 7.05–6.92 (m, 5H), 6.79 (dd, $J = 7.6$, 7.6, 1H), 6.68 (d, $J = 7.6$ Hz, 1H), 6.53 (brs, 1H), 6.47 (d, $J = 8.0$ Hz, 1H), 6.38 (d, $J = 8.0$ Hz, 1H), 2.19(s, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.2, 143.9, 142.7, 135.7, 130.3, 129.6, 128.76 125.6, 122.7, 120.3, 120.3, 120.2, 117.5, 109.1, 108.9, 105.1, 20.4, 16.9. IR (KBr, cm^{-1}): $\nu_{NH} = 3390$. MS (EI) 288. Anal. Calc. for $C_{20}H_{20}N_2$: C, 83.30; H, 6.99; N, 9.71. Found: C, 83.17; H, 6.79; N, 9.68%.

4.6.3. N-phenyl-4-[4-(4-toluidino)phenoxy]aniline (**36**)

The title compound was isolated as a beige solid in 76% yield after column chromatography using AcOEt/hexane 10:90 as eluant, m.p. 129 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (dd, $J = 7.6$, 7.6 Hz, 2H), 7.05 (2d, $J = 7.6$ Hz, 4H), 7.03–6.90 (m, 9H), 6.85 (dd, $J = 6.8$, 6.8 Hz, 2H), 6.53 (brs, NH), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.6, 144.2, 128.0, 129.8, 129.3, 120.8, 120.7, 120.2, 119.6, 119.3, 117.6, 116.5, 21.0. IR (KBr, cm^{-1}): $\nu_{NH} = 3392$. Anal. Calc. for $C_{25}H_{22}N_2O$: C, 81.94; H, 6.05; N, 7.64; O, 4.37. Found: C, 82.11; H, 6.16; N, 7.52%.

*4.6.4. N-(4-{4-[4-(4-anilinophenoxy)phenyl]phenoxy}-phenyl)-2-methylaniline (**37**)*

The title compound was isolated as a clear brown solid in 68% yield after column chromatography using AcOEt/hexane 15:85 as eluant, m.p. 133 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52–7.43 (m, 4H), 7.28–6.87 (m, 20H), 5.61 (brs, NH), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 157.9, 151.4, 151.1, 144.3, 142.2, 140.0, 139.2, 135.6, 135.5, 133.9, 131.3, 129.8, 128.6, 128.1, 127.2, 121.7, 121.0, 121.0, 120.7, 120.4, 118.5, 117.3, 114.6, 18.2. IR (KBr, cm^{-1}): $\nu_{NH} = 3400$, 3366. Anal. Calc. for $C_{37}H_{30}N_2O_2$: C, 83.12; H, 5.66; N, 5.21; O, 5.99. Found: C, 83.01; H, 5.57; N, 5.23%.

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References

[1] (a) D. Lednicer, Strategies for Organic Drug Synthesis and Design, Wiley, New York, 1998;
(b) R.O. Loutfy, C.K. Hsiao, P.M. Kazmaier, Photograph. Sci. Eng. 27 (1983) 5;
(c) G. D'Aprano, M. Leclerc, G. Zotti, G. Schiavon, Chem. Mater. 7 (1995) 33.

[2] For reviews on the Buchwald–Hartwig reaction, see: (a) J.F. Hartwig, Angew. Chem., Int. Ed. 37 (1998) 2047;
(b) B.H. Yang, S.L. Buchwald, J. Organomet. Chem. 576 (1999) 125;
(c) J.F. Hartwig, in: A. Ricci (Ed.), Modern Amination Methods, Wiley–VCH, Weinheim, 2000, pp. 195–262;
(d) A.R. Muci, S.L. Buchwald, Top. Curr. Chem. 219 (2002) 131–209.

[3] (a) N.M. Patil, A.A. Kelkar, Z. Nabi, R.V. Chaudhari, Chem. Commun. (2003) 2460;
(b) D. Mo, Q. Cai, Synlett (2004) 128;
(c) J.C. Antilla, J.M. Baskin, T.E. Barder, S.L. Buchwald, J. Org. Chem. 69 (2004) 5578;
(d) R. Hosseinzadeh, M. Tajbakhsh, M. Mohadjerani, H. Mehdinejah, Synlett (2004) 1517;
(e) Y. Yu, J. Srogl, L.S. Liebeskind, Org. Lett. 6 (2004) 2631.

[4] (a) M.M. Wienk, R.A.J. Janssen, J. Am. Chem. Soc. 119 (1997) 4492;
(b) T.D. Selby, S.C. Blackstock, Org. Lett. 1 (1999) 2053;
(c) S.I. Hauck, K.V. Lakshmi, J.F. Hartwig, Org. Lett. 1 (1999) 2057;
(d) Y.-K. Lim, S. Choi, K.B. Park, C.G. Cho, J. Org. Chem. 69 (2004) 2603.

[5] (a) K. Sato, M. Yano, M. Furuichi, D. Shiomi, T. Takui, K. Abe, K. Itoh, A. Higuchi, K. Katsuma, Y. Shirota, J. Am. Chem. Soc. 119 (1997) 6607;
(b) B.E. Koene, D.E. Coy, M.E. Thompson, Chem. Mater. 10 (1998) 2235;
(c) I.G. Hill, A. Kahn, J. Appl. Phys. 86 (1999) 2116;
(d) C. Biebeler, H. Antoniudis, D.D.C. Bradley, Y. Shirota, J. Appl. Phys. 85 (1999) 608.

[6] I. Kulszewicz-Bajer, I. Rogalska, M. Kurylek, New. J. Chem. 28 (2004) 669.

[7] (a) B. Gradel, E. Brenner, R. Schneider, Y. Fort, Tetrahedron Lett. 42 (2001) 5689;
(b) C. Desmarets, R. Schneider, Y. Fort, J. Org. Chem. 67 (2002) 3029;
(c) R. Omar-Amrani, A. Thomas, E. Brenner, R. Schneider, Y. Fort, Org. Lett. 5 (2003) 2311.

[8] (a) W.A. Herrmann, C.P. Reisinger, M. Spiegler, J. Organomet. Chem. 557 (1998) 93;
(b) V.P.W. Böhm, C.W.K. Gstöttmayr, T. Weskamp, W.A. Herrmann, J. Organomet. Chem. 595 (2000) 186;
(c) D. Bourissou, O. Guerret, F.P. Gabbaï, G. Bertrand, Chem. Rev. 100 (2000) 39;
(d) W.A. Herrmann, Angew. Chem., Int. Ed. 41 (2002) 1290.

[9] (a) J. Huang, G. Grasa, S.P. Nolan, Org. Lett. 1 (1999) 1307;
(b) G. Grasa, M.S. Viciu, J. Huang, S.P. Nolan, J. Org. Chem. 66 (2001) 7729;
(c) M.S. Viciu, R. Kissling, E.D. Stevens, S.P. Nolan, Org. Lett. 4 (2002) 2229;
(d) A.C. Hillier, G.A. Grasa, M.S. Viciu, H.M. Lee, C. Yang, S.P. Nolan, J. Organomet. Chem. 653 (2002) 69;
(e) M.S. Viciu, R.A. III Kelly, E.D. Stevens, F. Naud, M. Studer, S.P. Nolan, Org. Lett. 5 (2003) 1479;
(f) N. Marion, O. Navarro, R.A. III Kelly, S.P. Nolan, Synthesis (2003) 2590.

[10] S.R. Stauffer, S. Lee, J.P. Stambuli, S.I. Hauck, J.F. Hartwig, Org. Lett. 2 (2000) 1423.

[11] Y. Sato, R. Sawaki, M. Mori, Organometallics 20 (2001) 5510.

[12] (a) K. Selvakumar, A. Zapf, M. Spannenberg, M. Beller, Chem.-Eur. J. 8 (2002) 3901;
(b) K. Selvakumar, A. Zapf, M. Beller, Org. Lett. 4 (2002) 3031;
(c) R. Jackstell, A. Frisch, M. Beller, D. Röttger, M. Malaun, B. Bildstein, J. Mol. Catal. A: Chem. 185 (2002) 105;
(d) A.C. Frisch, A. Zapf, O. Briel, B. Kayser, N. Shaikh, M. Beller, J. Mol. Catal. A: Chem. 214 (2004) 231.

[13] (a) V.P.W. Böhm, T. Weskamp, C.W.K. Gstöttmayr, W.A. Herrmann, Angew. Chem. Int. Ed. 39 (2000) 1602;
(b) V.P.W. Böhm, C.W.K. Gstöttmayr, T. Weskamp, W.A. Herrmann, Angew. Chem. Int. Ed. 40 (2001) 3387;
(c) W.A. Herrmann, K. Olefe, D. Von Preysing, S.K. Schneider, J. Organomet. Chem. 687 (2003) 229.

[14] (a) C. Desmarets, S. Kuhl, R. Schneider, Y. Fort, Organometallics 21 (2002) 1554;
(b) S. Kuhl, R. Schneider, Y. Fort, Adv. Synth. Catal. 343 (2003) 341;
(c) S. Kuhl, R. Schneider, Y. Fort, Organometallics 22 (2003) 4184.

[15] M.G. Gardiner, W.A. Herrmann, C.-P. Reisinger, J. Schwartz, M. Spiegler, J. Organomet. Chem. 572 (1999) 239.

[16] (a) G. Thomas, Medicinal Chemistry, Wiley–VCH, Weinheim, 2000;
(b) E. Bellmann, S. Shaheen, S. Thayumanavan, S. Barlow, R. Grubbs, S. Marder, B. Kippelen, N. Peyhambarian, Chem. Mater. 10 (1998) 1668;
(c) C.S. Rondestvedt, J. Org. Chem. 42 (1977) 1786.